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(1 soft copy to Dr. Ullal; 1 hard copy to Ms. C. Lopez)

Re: Sixth Monthly Report on Pulsed Light Annealing #NDJ-2-30630-11 Mod 6

Dear Harin,

This letter comprises the six monthly technical status report for "CIGS Film Fabrication by Pulsed Light Annealing of Precursor Films", which is a task added as Mod 6 to ITN's subcontract #NDJ-2-30630-11, "Plasma-Assisted Coevaporation of S and Se for Wide Band Gap Chalcopyrite Photovoltaics", under the Thin Film Partnership Program. This letter describes work performed during the reporting period of February 15, 2003 through March 14, 2004.

Goals and Approach

The primary objective of this research effort is to demonstrate the production of high-efficiency thin-film CIGS solar cells on polyimide substrates by using high-rate heating from a super-intense pulsed light source. The heating rates to be investigated (millisecond time-scale) are at least two orders of magnitude higher than those reported in previous efforts to use Rapid Thermal Processing (RTP) to convert precursor materials to CIGS films for photovoltaics. Higher heating rates may be advantageous in that (1) thermal degradation of the substrate may be avoided with fast annealing and, (2) diffusion of gallium to the back of the film, which is a major limitation encountered in other CIGS RTP work, may be dramatically reduced. Goals of the present investigation are to determine the viability and challenges of using short (<50 ms) pulses from a super intense light source to:

- Convert sputter-deposited precursor films to chalcopyrite-phase CIGS.
- Improve co-evaporated CIGS electrical properties and thereby allow the use of lower deposition temperatures while retaining device performance.
- Develop a method for CIGS film production that is well suited for production scale-up and capable of producing efficiencies that match those achieved using high-temperature co-evaporation.

An additional goal will be to determine whether high-rate heating can effectively eliminate thru-film and lateral diffusion of elements during conversion of precursor structures to produce CIGS films with high front-side gallium content.

Activities

During the current reporting period, pulsed-light annealing was performed for the first time on a variety of CIGS precursor samples under a variety of conditions. Preparation for the treatments involved completing the fabrication of all the required precursor films, optically characterizing the films, performing additional temperature modeling, and calibrating the pulsed-light annealing system. Observations made so far on the samples subjected to pulsed-light treatments are promising, although we have not yet determined whether any of the films were converted to the chalcopyrite phase. This work is described in more detail below.

Precursor films fabricated for the first round of pulsed-light annealing experiments consisted of single-layer and double-layer precursor structures on both molybdenum-coated polyimide and molybdenum-coated stainless steel substrates. The single-layer films consisted of a single, 2-μm thick, homogenous layer of Cu, In, Ga, and Se with a slightly copper-poor and selenium-rich composition. The two-layer films contained the same amount of each element as in the single-layer films, but with the elements separated into an In-Ga-Se bottom layer and a Cu-Se top layer.

Reflectance spectra were measured on representative examples of each type of precursor sample. The spectra were then convolved with the spectra of the lamps used for the pulsed-light treatments to determine the overall reflectance for each type of sample. This information was then input into our temperature model to determine the pulse fluence (radiant energy per unit area) required to heat each type of precursor film to a temperature of ~560 °C. The fluence values from the modeling were used as starting points for the treatments. To calibrate fluence levels from the pulsed-light annealing system, a thin anodized aluminum disk was fabricated and characterized optically and thermally. The temperature increase in the disk when it was subjected to a pulse of light was then measured to determine the fluence of the pulse.

For pulsed-light treatments the precursor samples were mounted in either a "freestanding" configuration or a "backed" configuration. In the freestanding configuration, neither the front nor back of the sample was in contact with another object except at the edges where it was clamped. In the backed configuration, the sample was held in tension with its backside against a slightly curved brass piece to keep the backside of the sample at a relatively low temperature.

Several observations could be made immediately following the pulsed light treatment. When subjected to pulses of sufficiently high fluence, the two-layer films generally changed in color and texture strongly suggesting that a phase change had occurred. The single-layer films generally did not change their color or texture. At least part of the single-layer films delaminated upon treatment, whereas no delamination was observed for the two-layer films. In most cases, a redish residue appeared on the coverglass over the sample. The amount of residue ranged from being barely visible to being practically opaque depending on the treatment conditions. The residue could be easily wiped off of the coverglass. Higher fluence levels frequently caused the polyimide substrates to become somewhat deformed. The changes in the color and texture of the two-layer films could be obtained, however, at

fluence levels that were low enough to not deform the substrates. Uniformity in appearance across the film surface following pulsed-light treatment was generally good when the freestanding configuration was used and poor when the backed configuration was used. The poor uniformity with the backed configuration indicated that our setup did not provide sufficiently consistent thermal contact between the back of the sample and the backing block.

X-ray fluorescence (XRF) analysis was performed on the samples both before and after pulsed-light treatment. ITN has developed software for analyzing the XRF spectra from CIGS films. This software assumes that the CIGS film is homogenous throughout its depth. While our single-layer film samples should be homogenous, the two-layer samples were, by definition, not homogenous, at least prior to pulsed-light treatment. With the two-layer structure, the Cu x-ray intensity is higher and the In and Ga x-ray intensities are lower than they would be if the elements were mixed uniformly throughout a single layer. Our XRF analysis software therefore indicates a higher-than-actual value for the copper-to-group-III (Cu/III) ratio when applied to the XRF spectra of a two-layer film. If interdiffusion between the two layers takes place during pulsed-light treatment, the apparent Cu/III ratio indicated by XRF analysis should be lower after pulsed-light treatment than before. This was indeed observed for higher fluence values – and most strongly for the longer pulse time. In no case, however, was the decrease in Cu/III sufficiently large as to suggest that gradients in copper concentration through the depth of the film had been entirely eliminated.

XRF analysis was also used to examine the amount of selenium lost from the films during pulsed light treatment. Films were fabricated with approximately 5 to 10% excess selenium in order to compensate for possible evaporation during pulsed-light treatment. The observation of redish residues on the coverglass following treatment certainly suggests that some material was lost from films. XRF analysis, however, showed that, except in one case, the reduction in the ratio of selenium to metals in the film was never more than 6% (Figure 1).

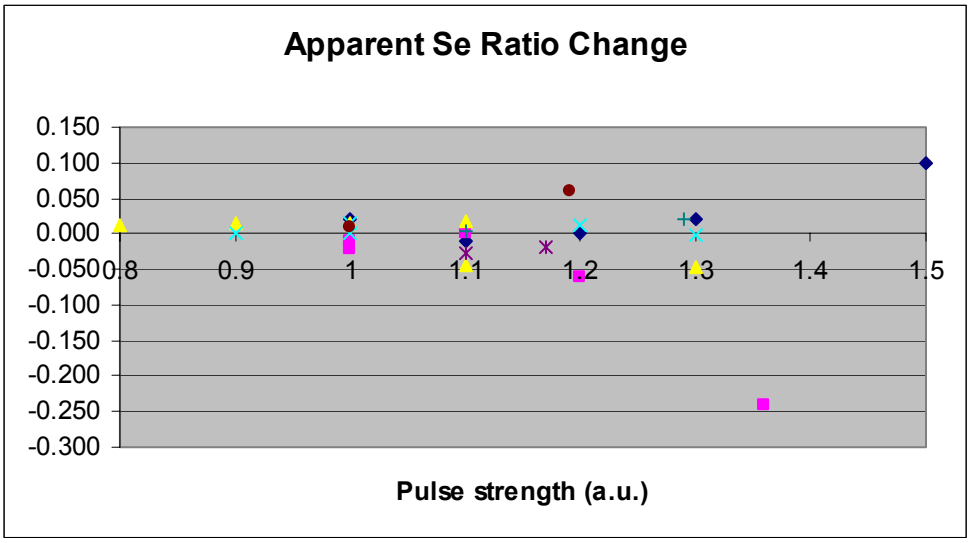

Figure 1: Change in apparent selenium-to-metals ratio as indicated by XRF. Differences in colors and shapes of markers indicate differences other than pulse strength such as film structure, pulse length, and mounting configuration.

Further characterization is planned for the samples treated in the first round of pulsed-light annealing experiments. X-ray diffraction (XRD) analysis will be performed to determine what phases are present in the films. If any samples are found to consist of mostly $Cu(In_xGa_{1-x})Se_2$ in the chalcopyrite structure, an attempt to make devices on these samples will be made. SEM will be performed to characterize morphology and grain structure. Auger or SIMS depth profiling may be performed to better characterize the amount of interdiffusion that occurred in the two-layer films.

Best Wishes,

Garth Jensen
Co-Principal Investigator
ITN Energy Systems

Cc: Ms. Carolyn Lopez; NREL contracts and business services